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Synthesis of Pentafluorosulfanylpyrazole and Pentafluorosulfanyl-1,2,3-triazole and Their Derivatives as Energetic Materials by Click Chemistry

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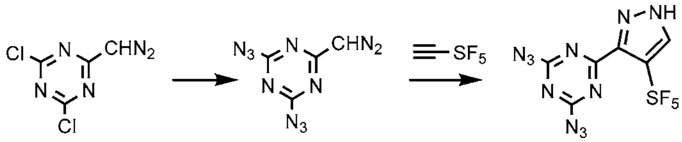
ABSTRACT



1-Pentafluorosulfanyl acetylene and its derivatives react with azide or diazomethane giving rise to an SF_5-substituted 1,2,3-triazole or pyrazole. The SF_5 group increases density remarkably and as a result enhances the detonation performance of the energetic materials relative to the CF_3 group.

Although introduction of pentafluorosulfanyl groups (SF_5) into organic compounds was initiated a half century ago,[1] a limited number of SF_5-containing compounds are available, being restricted by SF_5 sources or building blocks. Most recently, research in this field is booming with the development of new procedures for the preparation of aliphatic and aromatic SF_5 compounds.[2−6] It is believed that the SF_5 group may introduce unique properties into these organic compounds that include low surface energy, high chemical resistance, high thermal stability, high electronegativity, and hydrophobicity.[5e] A high dielectric constant and a greater electron withdrawing ability than the CF_3 group suggest that SF_5 may be an attractive alternative for the trifluoromethyl group.

The SF_5 group as a polar terminal group has produced a new class of liquid crystals that improved electrooptical

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properties over the $-CF_3$ group.[7] Pentafluorosulfanyl-containing compounds were also found to be superior for lowering aqueous surface tension vis-à-vis similar CF_3-containing analogues.[8] Polymeric SF_5-containing imides with low dielectric constants (2.51−3.00) have potential use in the electronics industry.[9] Polymers which contain the SF_5-moiety exhibit fluorinated surfaces with low wettability.[10] Other SF_5 compounds have found application as organic superconductor materials.[11]

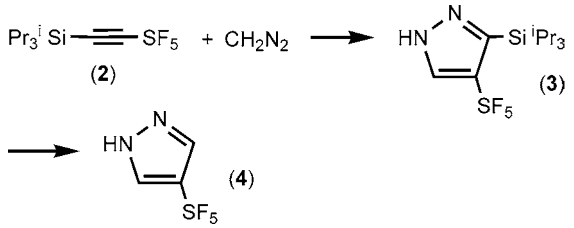
On the other hand, owing to the high density of the SF_5 group (2.57 g cm^{-3} for $-SF_5$ vs 2.25 g cm^{-3} for $-CF_3$, and 2.17 g cm^{-3} for $-NO_2$), SF_5 compounds have been used for energetic oxidizers.[12] 2-Polynitroalkyl-5-pentafluorosulfanylperfluoroalkyl-1,3,4-oxadiazole was found to be a new energetic plasticizer for a plastic bonded explosive, which does not migrate in fluoropolymer/nitroexplosives on storage.[13] Furthermore, considering bond energies of S−F, C−F, and Al−F (79, 107, and 158 kcal mol^{-1}, respectively) for weapon systems with metallized compositions of aluminum, conversion of S−F to Al−F will be more exothermic than a similar conversion of C−F to Al−F. Consequently, SF_5 explosives should be more energetic than their CF_3 analogues.

There are many known SF_5-alkyl, SF_5-polyfluoroalkyl, and derivatives of SF_5-aryl compounds.[2−6] However, compounds where the SF_5 group is incorporated in heterocycles are limited. We believe that the only SF_5 directly substituted heterocyclic compounds that have thus far been reported are SF_5-substituted furans[2a] and 5-SF_5-1,3-dithia-2,4-diazolium hexafluoroarsenate, prepared from the addition reaction of SF_5CN and $SNSAsF_6$.[14] Heterocycles where the SF_5 moiety is directly attached to the ring are a class of more intriguing compounds that would have potential bioactivity and could be used as intermediates to construct more complex molecules of interest.[15] Although the cyclization reaction of pentafluorosulfanylacetylene (SF_5CCH, **1**) with diazomethane was reported, the products were inseparable isomers of 4- and 5-pentafluorosulfanylpyrazole.[16] As our interests in high-density energetic materials continue, specifically in nitrogen-rich heterocycles, we report in this paper the synthesis of SF_5-substituted pyrazoles and SF_5-containing 1,2,3-triazoles and their derivatives by using “click chemistry”. Their detonation properties are also discussed.

1,3-Dipolar azide-alkyne cycloaddition, “click chemistry”, has been established as one of the most reliable means for the covalent assembly of complex molecules. It has enabled a number of applications in synthesis, medicinal chemistry, molecular biology, and material science.[17] Furthermore, a product of “click chemistry”, 1,2,3-triazole has a higher heat of formation than 1,2,4-triazole (270 kJ mol^{-1} vs 193 kJ mol^{-1} based on G3 calculation). But click chemistry involving pentafluorosulfanylacetylene (SF_5CCH, **1**) has rarely been reported for azide−alkyne cycloaddition reactions, which may be partly attributed to the lack of commercial availability and the less convenient manipulation for some since **1** is a gas at room temperature (bp 6 °C).[18]

We first reinvestigated the cycloaddition reaction of **1**[18] with diazomethane at 0 °C. The reaction proceeded rapidly, and resulted in isomeric SF_5-substituted pyrazoles, which is consistent with the literature.[16] Longer reaction time also leads to further N-methylation products. However, using the silylated derivative, 1-pentafluorosulfanyl-2-triisopropylsilylacetylene (**2**), and carrying out the reaction at −5 °C for a short time gave rise to a single isomer in good yield and selectivity. After desilylation with KHF_2 or tetrabutylammonium fluoride (TBAF) and recrystallization from chloroform several times, 4-pentafluorosulfanylpyrazole (**4**) was obtained (Scheme 1). The structure was established by X-ray diffraction, and is shown in Figure 1.[19] There are three independent molecules in the asymmetric unit. All have the same basic structural features ($S-C_{ipso}$ = ca. 1.75 Å, S−F = ca. 1.57 Å); however, the $S-C_{ipso}$ distance is shorter than the reported values of other SF_5 organic species (ca. 0.15−

Scheme 1. Synthesis of 4-SF_5-pyrazole



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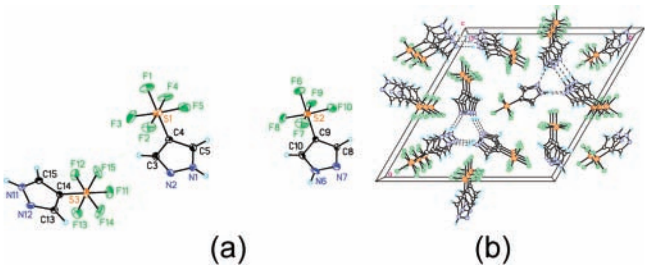
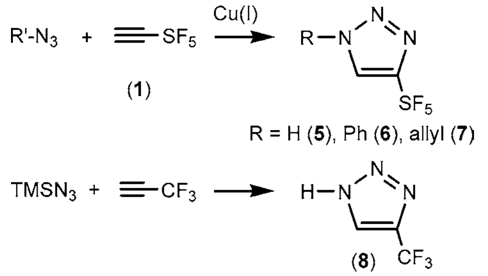


Figure 1. (a) Thermal displacement (30%) plot of the asymmetric unit of **4**. (b) Packing diagram of **4** viewed down the *c*-axis. Dashed lines indicate hydrogen bonding.

0.02 Å compared to the longest[3e] and shortest[3k] reported to date). The most notable feature of this structure is the hydrogen-bonding synthon, a spiral triangular stack parallel to the *c*-axis. Each unit of **4** in the cell forms independent hydrogen-bonded stacks through $N-H\cdots N$ interactions of ca. 2.8 Å.

The click chemistry of **1** with phenyl azides is straightforward. Under either typical "click chemistry" conditions[20] or without Cu(I) catalyst, the reaction of **1** with phenyl azide led to the desired 1-phenyl-4-pentafluorosulfanyl-1,2,3-triazole (**6**) in good yield (Scheme 2). But the presence of Cu(I) prepared in situ from $CuSO_4$/sodium ascorbic acid[20] expedites the reaction at low temperature and in short reaction time. Noteworthy, the reaction of excess $TMSN_3$ with **1** in CH_3CN or ethanol gave rise to 4-pentafluorosulfanyl-1,2,3-triazole (**3**) with concomitant desilylation. To our best knowledge, this is the first copper-catalyzed "click chemistry" involving gaseous alkynes. As a comparison, under the same conditions, no reaction occurred between **2** and $TMSN_3$. Similarly, reaction of $TMSN_3$ with 3,3,3-trifluoropropyne (CF_3CCH) produced 4-trifluoromethyl-1,2,3-triazole (**8**) in good yield. This was previously prepared from reaction of $TMSCHN_2$ with CF_3CN.[21] The structure of **5** was also confirmed by X-ray and is shown in Figure 2.[22]

Scheme 2. Synthesis of 4-SF_5-1,2,3-triazole and 4-CF_3-1,2,3-triazole by Click Chemistry



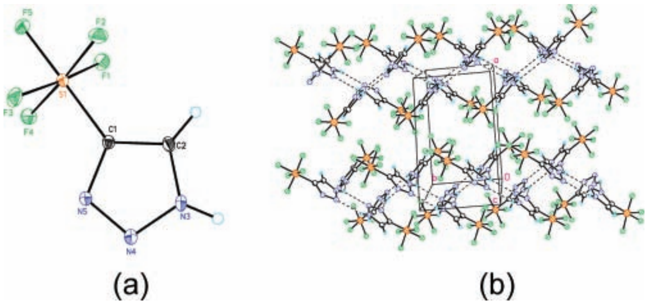


Figure 2. (a) Thermal displacement (30%) plot of **5**, (b) Packing diagram of **5** viewed down the *c*-axis. Dashed lines indicate hydrogen bonding.

Only one molecule is present in the asymmetric unit, and again the $S-C$ bond is relatively short at 1.775(2) Å. The $S-F$ bond lengths are similar to those found in **4** and other SF_5-containing organic molecules. The molecule is rich in hydrogen bonding, and the $NH-N$ interaction forms a two molecule criss-cross 2D stack parallel to the *b*-axis. This packing is more efficient than in **4** with a resultant increase in calculated density, 2.183 g cm^{-3} (90 K) and 2.08 g cm^{-3} at room temperature as measured with a gas pycnometer.

Three more SF_5 compounds (**10**, **12**, **14**) were also prepared which could be compatible with nitro-, heterocyclic-, or azide-explosives and fluoropolymers (Scheme 3). Density is one of the most important properties of energetic materials, since density is a critical factor that, according to a semiempirical equation suggested by Kamlet and Jacobs,[23] affects detonation performance, viz., detonation pressure (P) is dependent on the square of the density, and the detonation velocity (D) is proportional to the density.

These SF_5-containing compounds exhibit high densities ranging from 1.80 to 2.08 g cm^{-3}. The intermediates **9**, **11**, and **13** are also explosives candidates, but have low densities, e.g., 1.49, 1.60, and 1.54 g cm^{-3}, respectively. After cyclization with **1**, the densities of the corresponding products were greatly increased by 0.2−0.4 g cm^{-3}. In sharp comparison, when CF_3 was replaced by SF_5, the density of **5** increased by nearly 0.3 g cm^{-3} compared to that of **8**. This clearly demonstrates that the SF_5 group can remarkably boost the density of the energetic material. Most recently, we established empirical atom/group additivity to predict the

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[19] Crystal data for **4**: $C_3H_3F_5N_2S$, MW = 194.13, T = 90(2) K, trigonal, $P3(2)$, a = 18.2817(3) Å, b = 18.2817(3) Å, c = 5.1851(2) Å, V = 1500.79(7) Å^3, Z = 9, ρ_{calcd} = 1.933 Mg/m^3, μ = 0.519 mm^{-1}, reflections collected/ unique 21659/4600, R1 = 0.0482, wR2 = 0.1056 ($I > 2\sigma I$), GOF = 1.096.

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[22] Crystal data for **5**: $C_2H_2F_5N_3S$, MW = 195.13, T = 90(2) K, monoclinic, $P2(1)/c$, a = 10.5484(5) Å, b = 6.0792(3) Å, c = 10.0794(5) Å, β = 113.311(1)°, V = 593.59(5) Å^3, Z = 4, ρ_{calcd} = 2.183 Mg/m^3, μ = 0.588 mm^{-1}, reflections collected/unique 16635/1073, R1 = 0.0269, wR2 = 0.0742 ($I > 2\sigma I$), GOF = 1.074.

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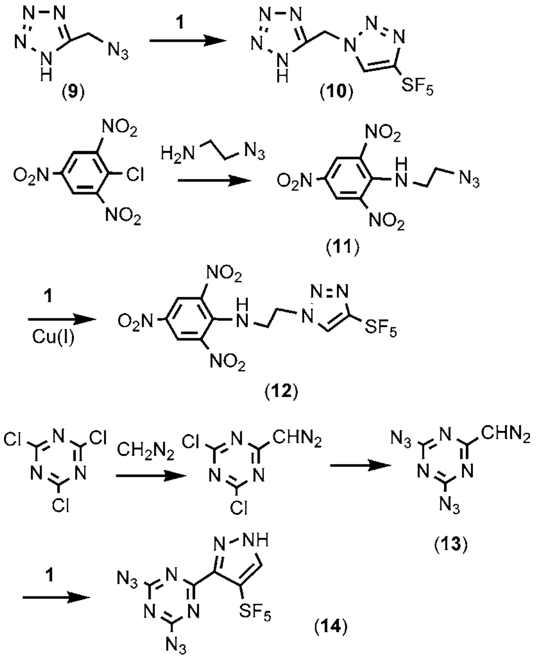
Scheme 3. Synthesis of SF_5-Containing Energetic Materials



density of energetic salts,[24] but the SF_5 group was not included initially. However, the volume of the SF_5 group was derived as 82 Å^3 based on nearly 10 organic crystals that are available in the Cambridge Crystallographic Data Centre files, which were used for the present estimation. The predicted densities are also listed in Table 1, which are reasonably close to the experimental value except for **4** for which density is overestimated. On the basis of atom/group additivity, a high-density polymorph may exist for this molecule.

These SF_5 materials are thermally stable. Heats of formation of the SF_5 compounds in the gas phase were calculated by using Becke's 3-Parameter, Lee−Yang−Parr functionals[25] at a basis set of 6-311G(d,p). The heats of formation in the condensed phase are in Table 1 where 20 kcal mol^{-1} was used as the enthalpy of sublimation for each compound. Detonation pressure (P) and detonation velocity (D) were also predicted with Cheetah 4.0. From Table 1, it can be seen that most of the SF_5-containing compounds exhibit a detonation performance comparable to that of TNT ($P = 20$ Gpa, $D = 6900$ m s^{-1}). The result clearly demonstrates that SF_5 compounds exhibit much better detonation properties than the CF_3 analogue (**5** vs **8**). The lesser performance of **4** is mainly attributed to its lower than expected density. Noteworthy, in the presence of metal powder, more energy will be released on detonation, which leads to much better detonation properties. Efforts to reduce the melting points so as to be useful as energetic plasticizers are underway.

Table 1. Melting Points (T_m, °C), Density (g cm^{-3}), Heats of Formation ($\Delta_f H°_{298}$, kJ mol^{-1}), Detonation Pressure (P), and Detonation Velocity (D) of the Energetic Materials

		density				
no.	T_m[a]	exptl	calcd[c]	$\Delta_f H°_{298}$	P[d] (GPa)	D[d] (m s^{-1})
4	141	1.83	2.00	−882.97	10.48	5487
5	99	2.08	2.07	−773.78	19.24	6945
8	83	1.79	1.83	−465.22	14.11	6518
10	132	1.89	1.90	−425.27	20.88	7107
12	176	1.80	1.82	−717.19	19.55	6931
14	128	1.85	1.88	−21.57	20.41	7464

[a] DSC under nitrogen gas, 10 deg/min. [b] Gas pycnometer. [c] Reference 24. [d] Calculated, Cheetah 4.0.

In summary, 1-pentafluorosulfanylacetylene and its derivatives react with azide or diazomethane giving rise to an SF_5-substituted 1,2,3-triazole or pyrazole. The SF_5 group can increase density remarkably and as a result enhance the detonation performance of the energetic materials relative to the CF_3 group. Calculations show that these SF_5-containing materials exhibit detonation properties similar to those of TNT.

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Supporting Information Available: X-ray crystallographic information files (CIF) are available for compound **4** and **5**, and the experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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